TITLE: COST-EFFECTIVE METHOD FOR PRODUCING SELF SUPPORTED PALLADIUM ALLOY MEMBRANES FOR USE IN EFFICIENT PRODUCTION OF COAL DERIVED HYDROGEN

QUARTERLY TECHNICAL PROGRESS REPORT

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DOE AWARD NUMBER:	DE-FC26-03NT41849
SUBMITTING ORGANIZATION:	SOUTHWEST RESEARCH INSTITUTE 6220 CULEBRA ROAD (78238-5166) P.O. BOX 28510 (78228-0510) SAN ANTONIO, TEXAS
OTHER TEAM MEMBERS:	COLORADO SCHOOL OF MINES IDATECH
SUBMIT TO:	NETL AAD DOCUMENT CONTROL BLDG. 921 U.S. DEPARTMENT OF ENERGY NATIONAL ENERGY TECHNOLOGY LABORATORY P.O. BOX 10940 PITTSBURGH, PA 15236-0940

SOUTHWEST RESEARCH INSTITUTE®

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DETROIT WASHINGTON, DC

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DISCLAIMER

ABSTRACT

In the past quarter, we have successfully released several compete membranes as thin as 3 microns from 12” diameter (113 sq. in.) rigid substrates with minimal pinhole defects. Samples taken from these membranes have been provided to Colorado School of Mines and Idatech for small scale testing and integration into a full-scale module, respectively. More than a dozen a 2 in. by 8 in. membranes have now been delivered to Idatech for testing in a prototype module. Idatech has successfully tested small membranes provided by SwRI to 100 psig and has measured flows of more than 420 scfh/ft^2.

Colorado School of Mines has tested additional membranes and in particular has performed additional measurements of membranes taken from previously tested lots. A permeation test cell has been modified to allow pressurization and testing of two membranes simultaneously. With guidance from Dr. David Sholl (Carnegie Mellon University) SwRI has also begun to prepare a number of ternary PdCu alloy membranes incorporating additions of tantalum, ruthenium, and rhodium. Tests on these membranes are currently underway at CSM.

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1.0 EXECUTIVE SUMMARY

Refer to abstract.

2.0 EXPERIMENTAL

Pd-Cu Membrane Deposition – Fabrication of 12-inch diameter membranes has continued this quarter. Almost a dozen of these large membranes have been produced with as few as six pinholes found over the entire membrane. Figure 1 show one of these specimens laid flat on a sheet of glass. In general, the pinholes are largely confined to the edges of the membrane. As part of preparing 2” x 8” membranes for Idatech, selected membranes were cross-sectioned and the thickness measured at 1-inch intervals across the diameter of the sample using a stylus profilometer.

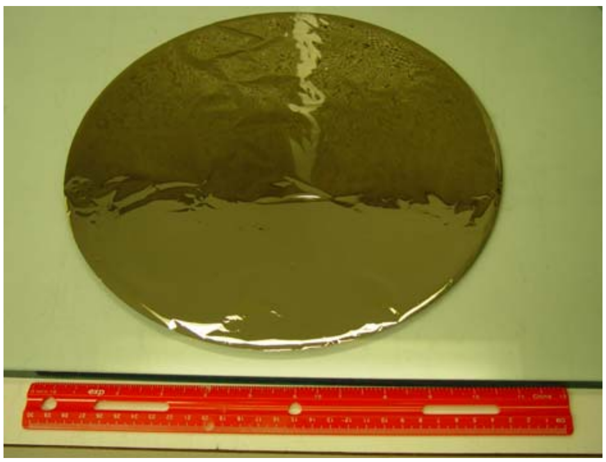
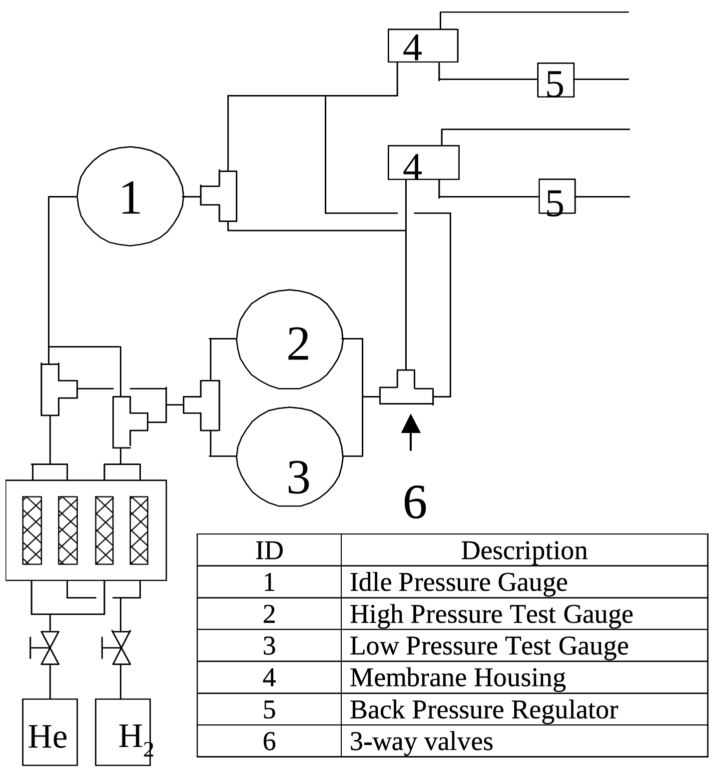


Figure 1. 12-inch low stress PdCu membrane approximately 4 microns thick.

A significant focus of this quarter’s activities was the preparation of several ternary alloy membranes. Recent work by Kamakoti and Sholl at Carnegie Mellon University using density functional theory to model the hydrogen transport through a membrane has suggested that alloy additions of 3-5 wt% of Rh, Ru, and possibly Ta could have a significant impact on the hydrogen binding and activation energies in PdCu alloys. In an effort to experimentally validate some of these predictions, small pieces of 99.9% pure Ru, Rh, and Ta were placed at different locations of the PdCu sputter target. Silicon witness samples were coated with 0.5-1.0 micron layers in short “tooling” runs and analyzed using energy dispersive x-ray spectrometry (EDX) to determine the composition. By adding or removing some of the Rh, Ru, or Ta pieces from the sputter target, the desired stoichiometry could be obtained. The release characteristics of Ru and Rh doped PdCu membranes was quite similar to the binary alloy while the Ta alloy was strongly adhered to the silicon backing. This problem was overcome by depositing a thin layer of pure Ta from a separate sputter source between two thicker layers of PdCu. The sample will be annealed before testing to diffuse the Ta throughout the membrane. A number of 1-ch and 2-inch square membranes of each alloy composition were provided to CSM for evaluation. We also hosted a visit by Dr. Steven Paglieri, who is conducting Pd alloy membrane research at Los Alamos National Laboratory. Several small membrane samples were provided to him for independent testing and evaluation.

***H_2 Testing* –** A new test apparatus has been plumbed and is able to run two membranes at a time. As shown in Figure 2, two test cells can be simultaneously pressurized with the outlet flow independently determined from separate back pressure regulators. There have been continued difficulties with the ceramic paper used to support the membrane and prevent damage when compressed between the graphite sealing gasket and the stainless steel support. Small punctures in the membranes have been observed when a pressure difference is applied. Attempts have been made to coat ceramic paper samples with boron nitrite and zirconium oxide, in and effort to produce a lower surface roughness and minimize damage to the membrane. Some porous stainless steel support discs have also been coated with zirconium oxide in an effort to eliminate the ceramic paper entirely.



ID	Description
1	Idle Pressure Gauge
2	High Pressure Test Gauge
3	Low Pressure Test Gauge
4	Membrane Housing
5	Back Pressure Regulator
6	3-way valves

Figure 2. Schematic of CSM dual-cell permeation test system

Membrane Testing and Module Development at Idatech – Idatech has inspected several experimental thin membranes in some instances discovered pinholes that were not revealed in light box tests at SwRI. While it is possible that pinholes developed during cutting of the membranes to size or during shipment, SwRI is reconsidering in QC approach for pinholes. Idatech will in also in the process of return selected samples for SwRI to re-inspect. Small 1-inch diameter active area foils were from a 5 um thick sample provided by SwRI. For initial pressure testing, the apparatus used was a permeation cell (Figure 3) heated in a furnace. The sample was pressurized to 1000 psig and operated without failure for several hours. The hydrogen flux was measured while at 400°C and under 100 psig H_2. Hydrogen flux was 421 SCFH/ft^2, which is consistent with estimated values based on the thickness. It is expected that in the coming weeks selected foils will be pressure tested to failure.

Figure 3. Idatech permeation cell used in initial pressure testing of thin membranes.

Figure 4 is a photograph picture of the full-scale prototype purifier designed to deliver 5 L/min of hydrogen. The first attempt to build up a reformer/membrane module using this hardware with a 6 um SwRI membrane failed during the gasket compression step of assembly. Figure 5 shows a photograph of the failed membrane. Inspection of the membrane outer edges (sealing region) shows many small tears, one of which extends into the active region of the membrane. This membrane was not annealed prior to assembly. No difficulties were encountered in assembling a reformer/membrane module a 5 um rolled foil which was leak tested without failure. In order to get a leak tight assembly, very high gasket loadings are required which in combination with a support material that is not flat can result in failure of an insufficiently flexible membrane.

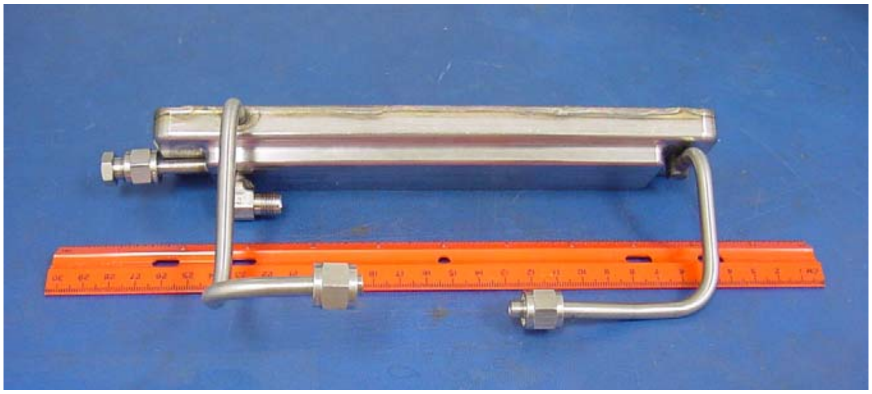


Figure 4. Idatech's prototype membrane module.

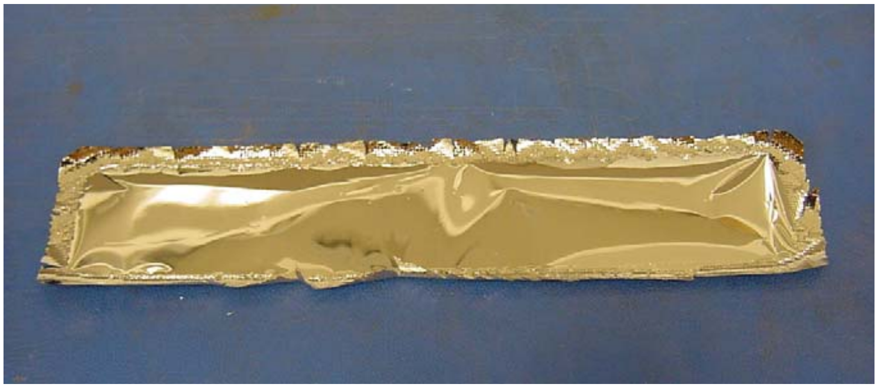


Figure 5. Photograph of compress membrane that developed a tear upon compression.

3.0 RESULTS AND DISCUSSION

3.1 Pd-Cu Membrane Optimization

Figure 6 is a graph of thickness as a function of position across the diameter of a representative 12-inch PdCu membrane. As the membrane material is built up on the silicon support, the sample is rotated and translated across the PdCu sputter target. The average thickness of this membrane is 5.3 microns with a thickness variation of approximately 20%. By using a larger sputter target or a different rotation/translation pattern, the thickness variation could be reduced to less than 5%. The EDX composition measurements for three representative ternary alloy membranes are shown in Table 2. Magnetron sputtering is uniquely suited for the rapid preparation and screening of new ternary alloys because the composition can be quickly changed simply by tiling different areas of material on the target.

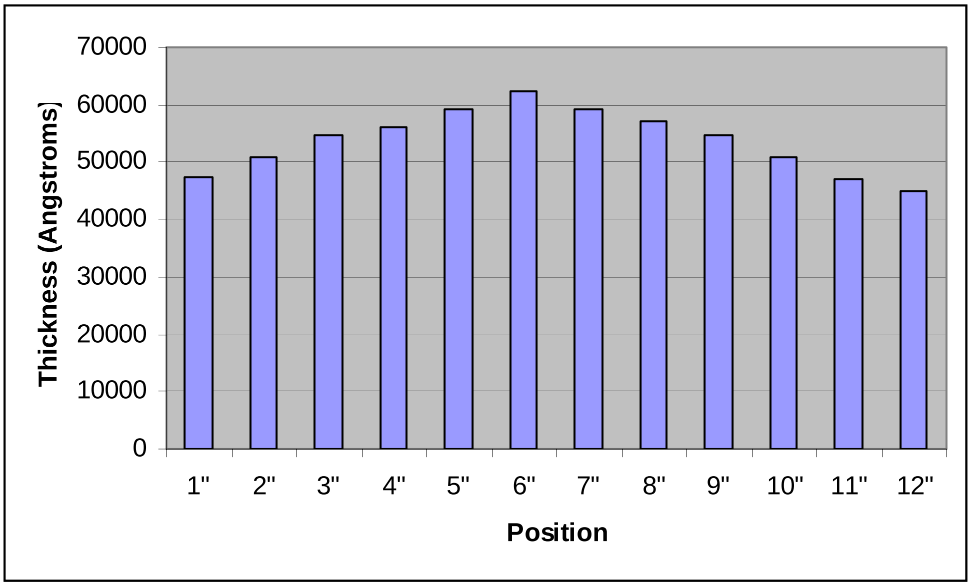


Figure 6. Measured thickness as a function of position across the diameter of a 12-inch PdCu membrane.

Table 1. EDX measurements of PdCuX ternary alloy membranes

Run #	Pd wt%	Cu wt%	X %
022106#1	56.6	37.5	5.9 Ru
030706#1	57.7	37.5	4.8 Ta
031406#1	54.4	38.4	7.2 Rh

3.2 H_2 Permeation Testing

Table 1 summarizes the most of the membrane tests that have been conducted at CSM over the past 6 months. While difficulties have been encountered with sealing the thinner membranes, tests on multiple samples from the same batch appear to exhibit reasonably consistent in performance. It should also be pointed out that the thickness measurements most commonly used a micrometer that can have difficulty measure extremely thin (<5 micron) membranes with sufficient accuracy. Two Pd-Cu-Rh ternary alloy samples are currently being tested. The flux of each, a 1-inch and a 2-inch, sample is 1.02 and 1.07 cm3(STP)/cm2.min at 400oC and 20 psig feed, respectively. These fluxes are adjusted for any helium leaks by assuming Knudsen flow but are lower than anticipated. The temperature has been raised to 525^{o}C to anneal the membranes in an effort to form a bcc phase structure.

Table 2. Summary of Membranes Tested at CSM through mid-March

Sample Number	Test Date	SwRI Pd %	Max Flux @ 400C & 20psi [$cm^3/cm^2 \cdot min$]	CSM Thickness [microns]	Permeance @ 400C [$cm^3(STP)/cm^2 \cdot s \cdot cmHg^{0.5}$]	Permeability @ 400C [$cm^3(STP) \cdot cm/cm^2 \cdot s \cdot cmHg^{0.5}$]
41805SI1	7/12/2005	59.47	42.7	6.00	0.105	6.30E-05
42005SI1	10/11/2005	60.35	43.2	6.80	0.111	7.55E-05
092805#2	1/13/2006	58.41	18.2	2.60	0.060	1.57E-05
092805#2	1/21/2006	58.41	3.2	2.60	0.011	2.86E-06
092805#2	3/8/2006	58.41	N/A	9.20	N/A	N/A
100405#2	1/12/2006	59.57	N/A	3.00	N/A	N/A
100705#1	2/21/2006	60.73	10.2	4.00	0.034	1.35E-05
100705#2	11/10/2005	59.48	66.9	9.00	0.142	1.28E-04
100705#2	2/6/2006	59.48	5.41	9.00	0.018	1.62E-05
100705#2	3/11/2006	59.48	10.6	9.00	0.035	3.16E-05
101005#1	10/23/2005	59.82	N/A	3.30	N/A	N/A
101005#1	10/24/2005	59.82	36.7	5.29	0.114	6.03E-05
101005#1	2/6/2006	59.82	N/A	3.30	N/A	N/A
101205#2	10/22/2005	59.85	N/A	9.00	N/A	N/A
101205#2	2/21/2006	59.85	N/A	2.50	N/A	N/A

3.3 Problems Encountered:

No insurmountable problems were encountered this quarter.

3.4 Plans for Next Reporting Period:

- SwRI will continue to prepare large PdCu alloy membranes for testing at Idatech. Specifically, effort will focus of controlling stress and minimize brittleness by pre-annealing large membranes prior to assembly in a module.
- SwRI will continue effort to QC membranes and minimize pinholes using improved sample preparation and inspection methods.
- CSM will continue testing ternary alloy membranes as well as additional membrane samples to support the large-scale test work at Idatech.
- Idatech will complete pressure and purification testing of at least one SwRI-manufactured membrane and test it in a prototype module assembly.
- Both CSM and Idatech will continue to investigate robust methods for sealing ultra-thin membrane without tearing.

4.0 CONCLUSION

Key achievements this past quarter include the first successful pressure and hydrogen permeation testing of small scale PdCu membranes at Idatech. The prototype module is complete and ready for assembly if we can fabricate a membrane that is resistant to tearing under high mechanical loads. In addition to fabricating several large, nearly pinhole-free membranes for use at Idatech, SwRI has fabricated novel ternary alloy membranes utilizing small addition of Ru, Rh and Ta. These samples are currently undergoing testing at CSM. CSM recently completed at modification to its setup allowing two membranes to be simultaneously pressurized and tested on hydrogen. They continue to investigate methods for annealing and sealing membranes to minimize tearing and fracture on assembly and pressurization.

5.0 REFERENCES

"Towards first principles-based identification of ternary alloys for hydrogen purification membranes," *Journal of Membrane Science, In Press*, Preeti Kamakoti and David S. Sholl.